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Electronic structure and magnetism of Sr_2RuO_4

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Abstract

We present the calculated low-energy electronic structure, in the meV energy scale, of Sr_2RuO_4 that is associated with the single-ion states of the Ru^{4+} ion. For description of the d electrons of the Ru^{4+} ion we take into account the orbital degrees of freedom, the spin–orbit coupling, and the extremely strong d–d electron correlations. These strong correlations lead to the formation of the highly correlated atomic-like $4d^4$ electron system. The derived electronic structure is different from that discussed at present in literature. We take recent Raman experimental data as experimental evidence for the existence of the discrete electronic structure.
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1. Introduction

Sr_2RuO_4 has recently received great scientific interest after the discovery that it superconducts, below 1.5 K, with coexisting weak ferromagnetism [1]. This fact calls for the need of a deeper theoretical understanding of the origin of both superconductivity and magnetism of 3d/4d oxides [2]. Most of ruthenate compounds are quite robust magnetically—$SrRuO_3$ exhibits ferromagnetism with $T_c = 160$ K and Ca_2RuO_4 exhibits antiferromagnetism below $T_N = 140$ K. Sr_2RuO_4 remains paramagnetic down to 1.5 K [3] while $CaRuO_3$ and $Sr_3Ru_2O_7$ remain paramagnetic to the lowest temperatures [4].

The aim of this paper is to present the calculated low-energy electronic structure of Sr_2RuO_4 resulting from single-ion states of the Ru^{4+} ion. For description of the d electrons of the Ru^{4+} ion we take into account the orbital degrees of freedom, the spin–orbit coupling, the local surroundings, and the very strong correlations among d electrons.

2. Theoretical outline

The Ru atoms in Sr_2RuO_4 are generally assumed in the literature to be in the tetravalent state, as $Sr_2^{2+}Ru^{4+}O_4^{2-}$. The Ru^{4+} ion has four d electrons in an incomplete outer shell. We assumed that they form the atomic-like highly correlated $4d^4$ electron system. In a zero-order approximation,

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the electron correlations within the incomplete d shell are accounted for by phenomenological Hund's rules that yield for the $4d^4$-electron configuration a ^5D term with $S = 2$ and $L = 2$ as the ground term. The ^5D term is 25-fold degenerate.

In the perovskite-like K_2NiF_4 structure the Ru^{4+} ions in Sr_2RuO_4 are situated in the octahedral surrounding of the O^{2-} ions. We have calculated the electronic structure resulting from the octahedral crystal–field (CEF) interactions and the intra-atomic spin–orbit coupling. We also studied the effect of distortions. Under the action of the crystal field with cubic symmetry, the ^5D term splits into the orbital triplet $^5T_{2g}$ and the orbital doublet ^5E_g with the latter being lower in the case of the octahedral ligand surroundings [5]. The 10-fold degeneracy of the ^5E_g subterm is further removed by the intra-atomic spin–orbit coupling and off-octahedral distortions. These distortions produce, at the place of the Ru cation, the multipolar terms in the electrostatic potential. They are accounted for by respective low-symmetry crystal–field terms. Calculations, revealing the many-electron states of the $4d^4$ system, their energies, and eigenfunctions in the 25-dimensional $|LSL_zS_z\rangle$ space, have been performed similarly to that in Ref. [6].

According to the QUantum Atomistic Solid-STate (QUASST) theory [7,8], developed by us, the discrete atomic-like electronic structure perseveres also when the paramagnetic atom becomes the entirety of a solid. These states, which allow excitations with energies comparable to the thermal energy, predominantly determine the magnetic and electronic properties of the whole compound.

3. Results and discussion

The calculated electronic structure, resulting from the octahedral crystal–field interactions and the spin–orbit coupling, is shown in Fig. 1. As is seen from this figure the combined action of the spin–orbit coupling and octahedral CEF interactions lead to the singlet ground state. This singlet, according to us, is the ground state of the Ru^{4+} ion and also perseveres in Sr_2RuO_4. It is responsible for the persistent non-magnetic state of Sr_2RuO_4
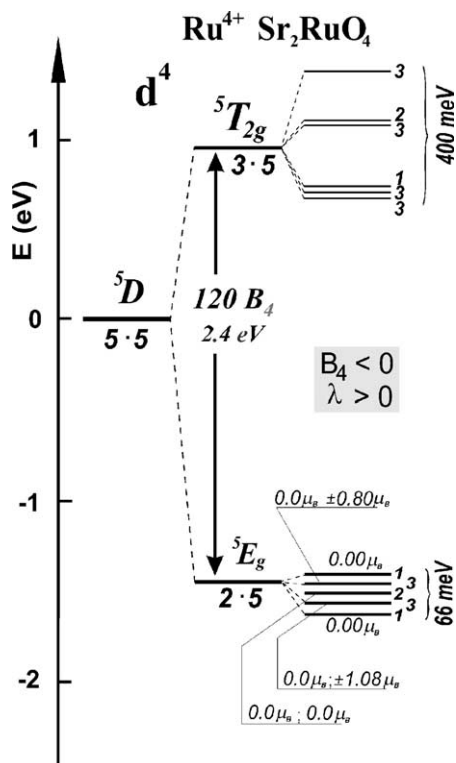

Fig. 1. The electronic atomic-like structure of Sr_2RuO_4 associated with the Ru^{4+} ion in the RuO_6 octahedron resulting from the octahedral crystal field and intra-atomic spin–orbit interactions.

down to 1.5 K. We believe that this singlet is the ground state in ruthenate compounds that do not order magnetically to the lowest temperatures.

The fine electronic structure obtained has a non-magnetic singlet ground state separated from the excited triplet state. The size of the singlet–triplet separation δ_{s-t} depends on the spin–orbit coupling λ_{s-o}. For a value of $\lambda_{s-o} = +500$ K, expected for the Ru^{4+} ion, it amounts to 68 K. δ_{s-t} increases to 207 K for $\lambda_{s-o} = +930$ K. This means that the larger the δ_{s-t} term the more difficult the magnetic state is formed. The computations have been performed for the octahedral CEF parameters $B_4 = -232$ K (-20 meV) in the crystal–field Hamiltonian $H_{CF} = B_4(O_4^0 + 5O_4^4)$. This value is consistent with the separation of 2.4 eV derived recently from X-ray absorption measurements [9] which we interpret as the T_{2g}–E_g separation of

Fig. 1. Here we would like to note that the result with the non-magnetic atomic state of the Ru^{4+} ion does not depend on the parameters chosen, i.e. the non-magnetic state is obtained for all sets of parameters, i.e. B_4 and λ_{s-o}, as long as the sign of both the parameters is kept. The non-magnetic state is, however, rather unstable. In general, the existence of so many close states encourages the development of the magnetic state, as we think proceeds in Ca_2RuO_4.

Lattice distortion causes splitting of the excited states and a shift which can lead to a drastic change in the low-energy electronic structure and the magnetic/non-magnetic ground state (Fig. 2). We would like to note that, despite the non-magnetic singlet ground state, a magnetic state could
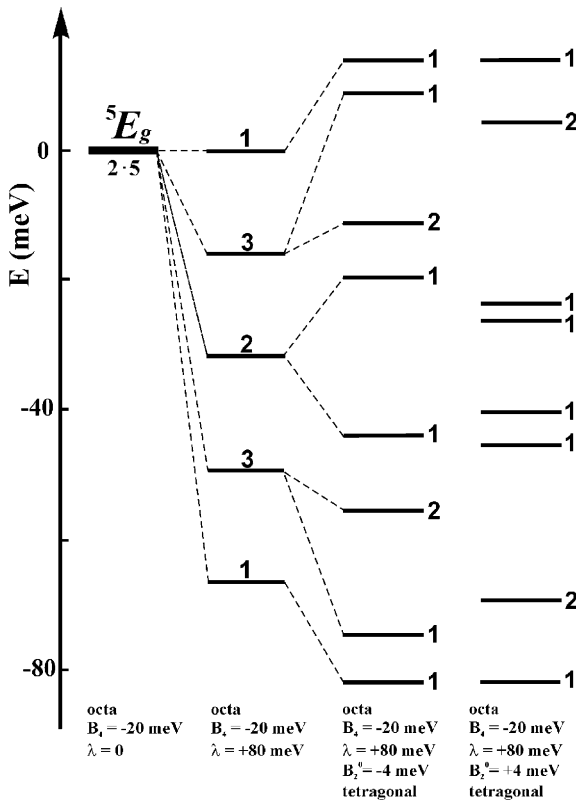

Fig. 2. The detailed low-energy electronic structure of the Ru^{4+} ion in the slightly-distorted RuO_6 octahedron related to the splitting of the ^5E_g subterm resulting from different types of the tetragonal distortion: $c/a > 1$ ($B_2^0 < 0$) and $c/a > 1$ ($B_2^0 < 0$). The case of $c/a < 1$ ($B_2^0 > 0$) occurs in Sr_2RuO_4.

be formed—such singlet–singlet ordering is well known in Pr compounds [10]. Such a magnetic state is relatively weak, which is exactly the case for Sr_2RuO_4. Our calculations indicate that the tetragonal distortion is much more effective in the lowering energy of the system then a trigonal distortion (the tetragonal distortion is, somehow, favored by the K_2NiF_4 structure). This agrees nicely with the experimentally observed tetragonal distortion in Sr_2RuO_4. Experiments have determined that the distortion is such that the apical oxygen ions are expanded along the c axis ($c/a > 1$).

At zero temperature only the lowest state is occupied causing non-magnetism of Sr_2RuO_4. With increasing temperature the higher states become thermally populated as given by the Boltzmann-statistical function. We expect a Schottky-like contribution to the temperature dependence of the specific heat. Due to the large number of involved states this contribution will be very broad, but its presence should be visible in large entropy.

For the ideal octahedron the susceptibility above 150 K mimics that given by the Curie(–Weiss) law, in spite of the non-magnetic ground state, and in spite of the presence such a complicated discrete electronic structure. This complicated discrete energy structure, with 10 low-lying states in quasi-octahedral surrounding, is the physical reason for very different ground states and non-trivial magnetic and electronic properties in ruthenates, according to us. The distortions cause (i) anisotropy of the paramagnetic susceptibility and (ii) quite unusual behavior with substantial violation of the Curie–Weiss behavior.

The ground state function for the $c/a > 1$ case (our ab initio calculations show that $c/a > 1$ corresponds to $B_2^0 < 0$), realized in Sr_2RuO_4, is given as

$$\Psi_{GS\rangle} = 0.66|x^2 - y^2, +2\rangle + 0.66|x^2 - y^2, -2\rangle + 0.31|z^2, 0\rangle$$

where the first part of the bracket is related to the orbital part, and the second part to the spin number. The orbital functions $x^2 - y^2 = 1/\sqrt{2}(|+2\rangle + |-2\rangle)$ and $z^2 = |0\rangle$ are denoted similarly to the conventional single-ion orbitals. However, it

should be noted that here they correspond to the highly correlated $4d^4$ system, that is also described by $L = 2$, resulting from the second Hund's rule.

4. Conclusions

The low-energy electronic structure, in the meV scale, of Sr_2RuO_4 has been calculated. It is associated with the atomic-like states of the Ru^{4+} ion. We take into account the spin and orbital degrees of freedom and extremely strong d–d electron correlations which lead to the formation of a highly correlated atomic like $4d^4$ electron system. The derived electronic structure is different from that discussed at present in literature (e.g. [2,3]), which are single electron in nature with rather weak correlations.

The weakly magnetic state of Sr_2RuO_4 is associated with the non-magnetic singlet ground state of the Ru^{4+} ion being situated in a quasi-octahedral crystal field. This atomic-scale singlet non-magnetic state can be revealed theoretically provided the spin–orbit coupling is correctly taken into account. Despite the singlet ground state a weak magnetic state can be formed. The present approach, based on the general symmetry and well-known physical mechanisms, offers a much simpler explanation for the nonmagnetic state of Sr_2RuO_4 than that discussed thus far in the literature. In our QUASST approach the CEF interactions play a very important role. Although they are strong, they are not strong enough to completely destroy the 4d shell and contradict Hund's rules. We are convinced that the presented approach to the low-energy electronic structure can be applied to other Ru^{4+} ion compounds. It is, however, necessary to remember that the electronic structure of the pentavalent Ru ion is completely different. According to us some excitations detected recently in the Raman spectroscopy of Sr_2RuO_4 and reported in Refs. [11,12] are those related to the fine electronic structure shown in Fig. 2.

In this contribution we would like to emphasize the importance of the orbital magnetism, and the orbital quantum number in particular, due to the fact that the 3d/4d magnetism is commonly discussed as a spin-only magnetism. Our studies indicate that the intra-atomic spin–orbit coupling should be taken into account in the description of the electronic structure as well as the magnetic and electronic properties of 3d-/4d-atom containing compounds.

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